Modification of Polymer support with Bound Surfactants

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by

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CERTIFICATE

It is certified that the work contained in the thesis entitled Modification of Polymer Support with Bound Surfactants by Rangalal Das, has been carried out under my supervision and that work has not been submitted elsewhere for a degree.

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ABSTRACT

In the epoxidation of allyl chloride with hydrogen peroxide, the previous work cleary shown that catalysis of H_2O_2 becomes a prominant reaction reaction due to polymer support. In this work we have modified the polymer surface by reacting with 12-hydroxy stearic acid complexing its carboxylic moity with heteropoly acid. The catalyst thus developed was then used for epoxidation reaction and shown to minimize the autolysis of H_2O_2 . In addtion to this polymer support forced the HPA at the interface this way promoting the reaction.

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Rangalal Das

CONTENTS

INTRODUCTION

Oxidation is one of the most important reactions industrially and epoxidation of ethylene and propylene is a convenient method of introducing oxygen this way making these molecules highly reactive. In fact ethylene and propylene oxides are important intermediates from which several chemicals are produced commercially as shown in Figure 1.1 [1].

In order to carry out epoxidation reaction, a double bond of olefin is required along with a suitable labile oxygen of a reagent as shown in

$$\diagup C = C \diagdown \xrightarrow{\text{[Reagent] or}\atop\text{[Catalyst/Oxidant]}} \diagup C \overset{O}{\diagup\diagdown} C \diagdown \qquad (1.1)$$
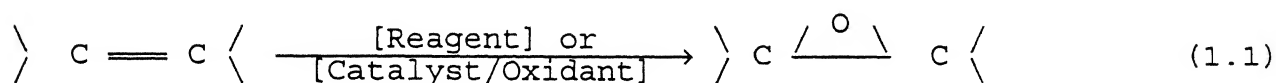
Traditional methods of epoxidation had always been associated with multistep reactions and a number of co-products making the process uneconomical. For example, ethylene is epoxidized by reacting ethylene with hypochlorous acid as,

$$CH_2 = CH_2 + HOCl \longrightarrow HO-CH_2-CH_2-Cl \qquad (1.2)$$
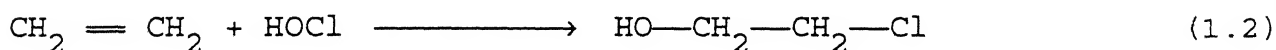
This is gas-liquid reaction and the final conversion depends upon the efficiency of embanking. The product is then dehydrochlorinated by refluxing it with $Ca(OH)_2$ as follows

$$2HO-CH_2-CH_2-Cl + Ca(OH)_2 \longrightarrow 2CH_2 \overset{O}{\diagup\diagdown} CH_2 + CaCl_2 + 2H_2O \qquad (1.3)$$

→	Glycols	Plasticizer
→	Ethylene Glycol	Antifreeze agents, explosives, plastic
→	Polyethylene Glycol	Plasticizer, Textile Auxiliaries, Paints, Wasex
→	Morphholine	Detergent substances, Medicinal product and bactericides
→	Alkylphenyl Polyethylene Glycol Ethers	Detergents
→	Ethanolamines	Soaps, Creams, wetting agents

:hylene Oxide → Chroline — Medicinal Products, Fooder additives Vitamin B

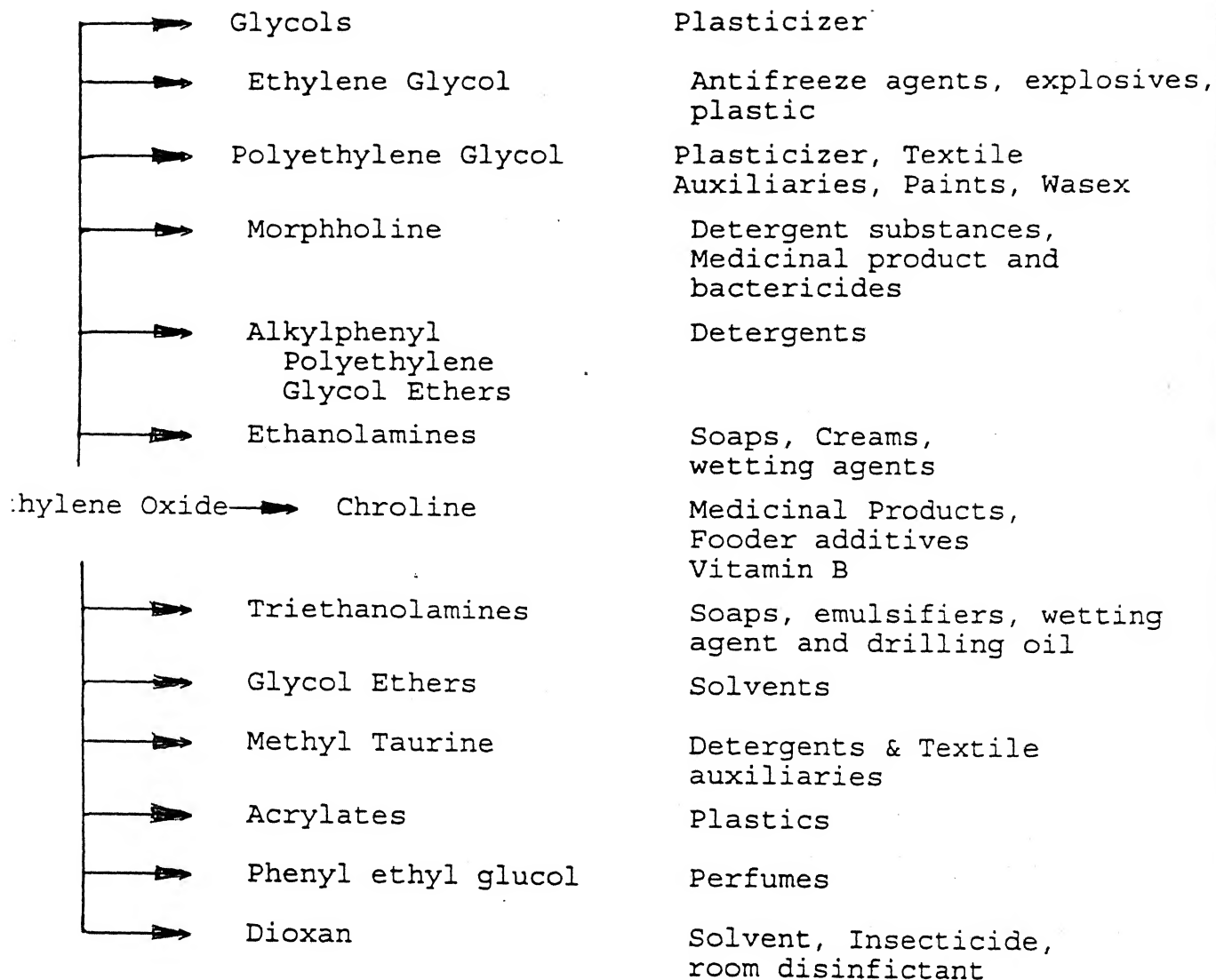|		
→	Triethanolamines	Soaps, emulsifiers, wetting agent and drilling oil
→	Glycol Ethers	Solvents
→	Methyl Taurine	Detergents & Textile auxiliaries
→	Acrylates	Plastics
→	Phenyl ethyl glucol	Perfumes
→	Dioxan	Solvent, Insecticide, room disinfictant

Fig 1.1   Products Made from Ethylene Oxide

8

Evidently, the separation of the final product is difficult and the yield of final product is smaller and as a result of this ethylene oxide is rarely prepared this way and commercially one employs a catalytic route.

Industrially ethylene oxide is produced using Shell process in which oxygen and ethylene are contacted in a tubular reactor having silver gauze. The reaction is highly exothermic and per pass the contact time is kept small in order suppress the formation of side product carbon dioxide. In the workup section ethylene oxide is scummed using water and than distilling subsequently. Before recycling ethylene, the CO_2 is separated after compressing the gas mixture. Similarly, propylene oxide is produced using molybdenum as catalyst and for this case, CO_2 produced by side reaction could be as high as 30% and sometimes one uses dichloromethane in 1 ppm concentration level in order to suppress this side reaction.

As the size of the olefin molecule increases, the higher temperature of reaction increases the extent of side reaction forming CO_2. As a result of this, the use of catalyst and the oxidizing agent other than dioxygen are desirable. In the literature, epoxidation reaction has been extensively studied for different reagents and catalyst oxidation systems and has been reviewed recently by Shaneeth et al[2]. The literature search reveals that the catalytic epoxidation is preferred over the noncatalytic one because the former gives greater selectivity of the product and greater control over the reaction.

It has been found that the activity of the catalyst is greatly influenced by the nature of the ligands. In presence of proper ligand coordination, the ability of transition metals to switch between two different oxidation states is considerably enhanced. Then selection of the ligands is important, is specific to the reacting medium and should not be degraded. However several organic ligands are unstable and in an effect to overcome this problem; people have used polyhalogenated prophyrins [3,4], inorganic polyanions (eg. heteropolyacids, HPA) and zeolite lattice [5,6,7,8]. The heteropolyacids are poly metal oxo compounds with metal being V, W or Mo and one or more of atoms of phosphorus. These have stable and are in a cluster, called Kezgin structure, eg., $H_3XM_{12}O_{40} \cdot xH_2O$ where X is P or Si and M is V, W or Mo.

Olefin epoxidation using hydrogen peroxide as the oxidizing agent is a biphasic reaction in that olefin lies in the organic phase and hydrogen peroxide in the aqueous phase. This necessitates transfer of the active complex across the phase boundaries for which quaternary ammonium or phosphonium salts are generally used. The epoxidation reaction can be achieved only by means of catalysts based on oxides of metals belonging to VA, B and VI A, B groups of periodic table [9,10]. Virtually anhydrous conditions were necessary for the early successes [11,12] as a result of which 90% H_2O_2 was used. Venturello and coworkers [13] developed a new method of epoxidation using dilute solutions of hydrogen peroxide. They used a combination of sodium tungstate

and sodium meta phosphate in presence of a quaternary ammonium salt as the catalyst. Using Heteropoly acid as the catalyst precursor, Ishii et al. [14,15] arrived at similar results. It was observed that only those heteropoly acids which lose their Keggin structure in presence of excess H_2O_2 could catalyze the epoxidation [16]. Since then, several catalytically active anionic species have been synthesized in the form of quaternary ammonium salts [13,17]. Hill and coworkers [18] confirmed that the anionic species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is the most important epoxidizing agent in Ishii-Venturello system. In the proposed scheme formation of epoxide utilizing H_2O_2 occurs as shown in Figure 1.2.

In order to characterize the catalyst, people use turnover rate which is defined as the number of product molecules formed per active catalytic area per unit time. As opposed to this turnover number is the product of turnover rate and total reaction time. This signifies the number of product molecules formed per active catalyst area in its life time. For a reaction to qualify as catalytic, a turnover number should be of the order of 10^2 or larger [19,20]. In the above system a maximum turnover of 500 (mole of epoxide/mole of catalyst) has been observed and the catalyst undergoes irreversible degradation eventually.

Figure 1.2 : Schematic Representation of the Evolution of the Active Catalyst and the Formation of Epoxide

When hydrogen peroxide is the oxidizing agent the catalyst gives homolytic cleavage of O-O and O-H bonds of H_2O_2 leading to the formation of dioxygen and water as waste side reaction[21-26,6]. The minimization of side reaction of H_2O_2 has been difficult and limits the choice of metal selected for catalysis. It has been observed that the electron poor d^o * complexes of Ti, Mo, W and Re satisfy this prequisite [27]. Among these the best results are obtained when $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is used. They are found not to dismute H_2O_2 appreciably and are oxidatively stable [13,7,28] in catalytically homogeneous biphasic reactions. The catalyst is prepared as a quaternary ammonium or phosphonium (together called onium) salt having the following formula, $[(C_8H_{17})_3NCH_3]_3^+ \{PO_4[O(O_2)]_4\}^{3-}$. More example on the variations of this are given in Table 1.3 [2] These onium cations are known to facilitate phase transfer reaction as follows [13,14,7,17]:

Aueous Phase $\quad Q^+Y^-\ +\quad R\!-\!X\quad\longrightarrow\quad R\!-\!Y\quad +\quad Q^+X^-$
$\qquad\qquad\qquad\qquad\qquad$ (Substrate) $\qquad\qquad$ (Product) $\qquad\qquad$ (Onion salt

Orrganic Phase $\quad Q^+Y^-\ +\quad Na^+X^-\quad\rightleftharpoons\quad Na^+Y^-\quad +\quad Q^+X^-$)
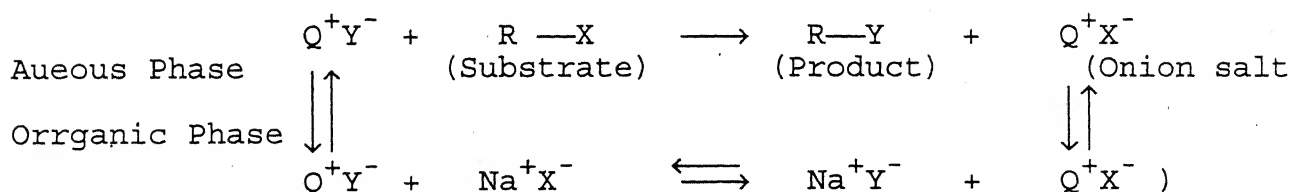
Figure 1.2 : Mechanism of Phase Transfer Catalysis

This substitution reaction is made possible by the presence of Q^+X^- (quaternary onium salt) which transports aqueous phase soluble Y^- to organic phase [29,30].

Since HPA, has been reported to be a good epoxidation catalyst, it was decided to examine this system in detail. Since the sodium salt of HPA dissolves in water, after reaction is carried out it, the catalyst is not recoverable. In view of this, it was decided to bind the HPA cluster molecule to a suitable support which does not dissolve in the reaction mass. Heterogeneous catalyst has gained considerable importance because the catalyst can be recovered. In addition to this they give a better control over the structure of the catalytically active species which as a consequence lead to higher activity, selectivity and life span [31]. Heterogeneous catalysts generally have two parts: an inert support material (called carrier) having high surface area attached to a catalytically active species. Virtually any inert solid which has a surface area of the order of 10^1 - 10^2 m^2/g can be used as a support [32], and can be an inorganic (like silica, alumina etc.) or organic (like styrene - divinyl benzene copolymer) in nature.

The metal species giving catalytic action can be bound to the support by physical sorption or by chemical bonding. The latter can further be classified as covalent, coordinative or ionic. Most of the time a chemical bonding requires an appropriate functional group to be generated on the support because the latter

do not have any or these present on their surfaces. Functional groups not only form the sites for catalyst complexation but also act as the ligand structure surrounding the metal, this way facilitating the required activity. In many situations it is necessary to keep the catalytically active species away from the surface by giving 'enough length' (number of atoms, mostly carbon) between the surface and the active species. This is generally known as spacer effect.

The work of Shaneeth consisted of binding onium salt of heterpoly acid on functionalized supports and using this for epoxidation of allyl chloride to epichlorohydrin using hydrogen peroxide. It was found that as such the onium salt is inactive and it is necessary that it should be converted to an active complex $\{PO_4[WO(O_2)_2]_4\}^{3-}$ by treating it with H_2O_2 before it is precipitated using onium cation. In situ catalyst system should slightly higher activity under reflux condition. Two functinalized supports viz polystyrene - divixylbenzene copolymer beads and silica gel were prepared and on their quaternary onium groups were prepared. It was shown that their degree of functionalization played a critical role in loading of the supported catalyst. Their work indicated that cationic surfactant type ion pairing supports would give more appropriate material for holding the HPA. For this purpose, a linear cationic surfactant, polymer, a crosslinked surfactant polymer and/or a cationic surfactant macromolecule attached on polymer beads was proposed.

In this work, we wished to modify styrene divinylbenzene copolymer beads by chemical bonding a surfactant on its surface. The surfactant molecule for this purpose was chosen to 12-hydroxysteric acid and its carboxylic group was reacted with choline chloride. The copolymer beads were first reacted with monochloroacetic acid and the modified surfactant was reacted with the beads, which served as a support for HPA. The catalyst thus developed was used for epoxidation of allyl chloride. The study of this reaction gave encouraging results.

CHAPTER - 2

EXPERIMENTAL SECTION

FLOW SHEET OF EXPERIMENTAL SECTION

(P)—⬡

    $Cl-CH_2CO_2H$ 12-Hydroxy Steric Acid

    $SnCl_4$ $SOCl_2$

    [Reflux] 80°C   12-Hydroxy Steroyl chloride

    [Acetonitrile solvent] $NH_2CH_2CH_2NH_2$ (excess)

(P)—⬡— CH_2CO_2H 12-Hydroxy Steroyl 1,2-
                                       amide amine

                                Chloro choline-
                                 chloride

                        Quaternary Ammonium salt
                        of 12-hytdroxy steric acid

                      (1,2-dichloromethane solvent,
                      40°C, reflux)

Polymer bead supported, Quaternary ammonium salt of 12 hydroxy

steric acid

                        [Phosphotungstic acid
                        40°C, 1-2 dichloro methane
                        solvent)

Polymer suported - Quaternary ammonium salt of Phosphotungstic

acid (Catalyst)

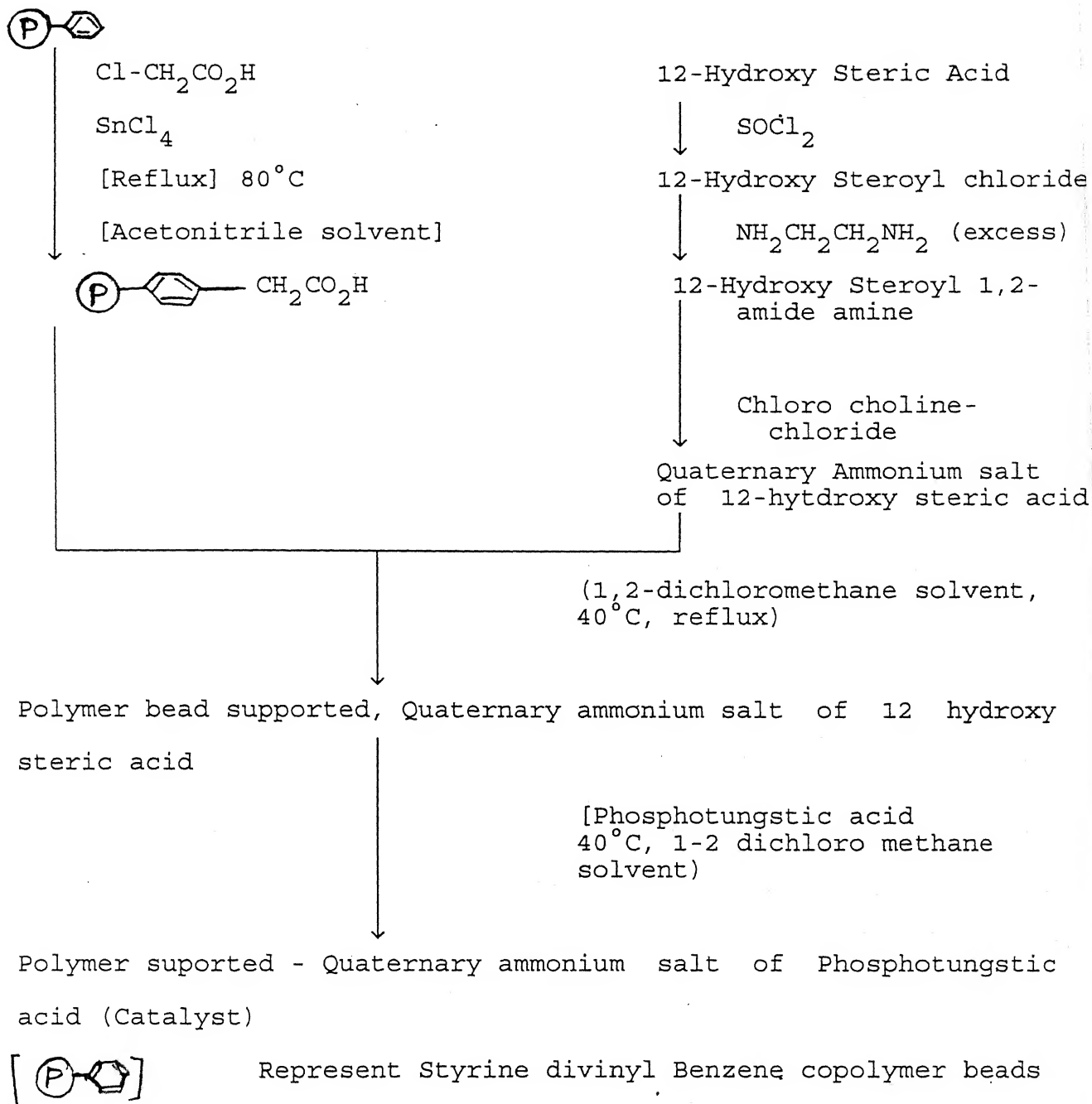[(P)—⬡]   Represent Styrine divinyl Benzene copolymer beads

Figure 1.3

SYNTHESIS OF THE HETERO POLY ACID - PHOSPHOTUNGSTIC ACID

Phosphotungstic acid was prepared according to literature procedure [33], In this sodium tungstate ($Na_2WO_4.2H_2O$, 100 gms, 0.3 mol) and disodium meta phosphate ($Na_2HPO_4.2H_2O$, 16 gm, 0.09 mol) dissolved in 150 ml. of boiling water. Concentrated hydrochloric acid (80 ml) was added 10 min in dropwise with constant stirring. Phosphotungstic acid begins to separate when about half of the acid has been added.

$$Na_2WO_4 + Na_2HPO_4.2H_2O \xrightarrow[\text{acidic medium}]{} 24WO_3, 2H_3PO_4, 48H_2O \qquad 2.1$$

In order to purify the precipitated acid, it was mixed with methanol (free from reducing impurities) and the solution was heated at low temperature $30-40^0C$. The phosphotungstic acid begins to separate. Then it was filtered and dried at room temperature. The yield of phosphotungstic acid was about 60 gms.

SYNTHESIS OF THE QUATERNARY AMMONIUM SALT OF 12-HYDROXY STEARIC ACID :

2(a) PREPARATION OF 12-HDROXY STEROYL CHLORIDE :-

Preparation of 12-hydroxy steroyl acid chloride was done as fallows. 5 gm (0.017 mol) of 12-hydroxy stearic acid was added to approximately 2c.c of thionyl chloride (0.017 mol) and the mixture was stirred for 8-10 hrs at room temperature. The 12-hydroxy steroyl acid chloride was formed.
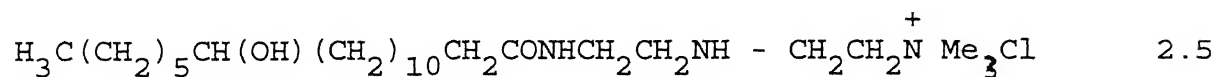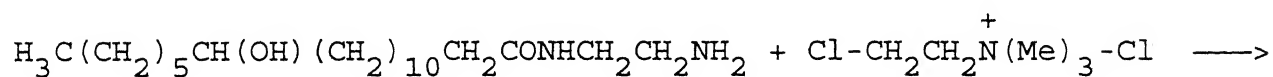
$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}CO_2H \quad + \quad SOCl_2 \text{------>}$$

$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}COCl \qquad\qquad 2.2$$
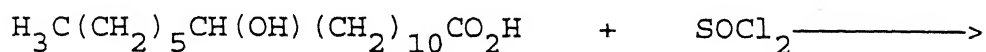
As the product is formed, it dissolves in the reaction mass and the solution turns black.

2(b) PURIFICATION & REMOVAL OF EXCESS THIONYL CHLORIDE (IF PRESENT)

The reaction mixture obtained above was mixed with 1-2 dichloro methane solvent (50 c.c). It was first refluxed at 40^0C for 6-8 hrs. after refluxing 20 ml of n0hexane was mixed. This mixture washed several times with distilled water for removing free $SOCl_2$.

2(c) PREPARATION OF 12-HYDROXY STEROYL 1,2 AMIDE AMINE :

The purified steroyl chloride (which is a liquid) of 5 gms of stearic acid was added sloely to 100 ml of ethylene. A precipitate of the product appears rightaway which was separated through filtering. The amount of the product was about 6 gms and it is formed through the following reaction.

$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}CH_2COCl + NH_2CH_2CH_2NH_2 \text{(excess)} \longrightarrow$$

$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}CH_2CONH-CH_2CH_2NH_2 \longrightarrow 2.3$$

$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}CH_2COCl \text{ (excess)} + NH_2CH_2CH_2NH_2 \longrightarrow$$

$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}CH_2CONH$$
$$\diagdown CH_2$$
$$CH_2$$
$$\diagup$$
$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}CH_2CONH$$

$$\longrightarrow 2.4$$

Formation of 12-hydroxy steroyl 1,2 amide,amine was confirmed by I.R. spectroscopy. The frequency of free O-H (3400 cem^{-1}), CONH (1625 cem^{-1}) obtained which is agreement with literature value [37]

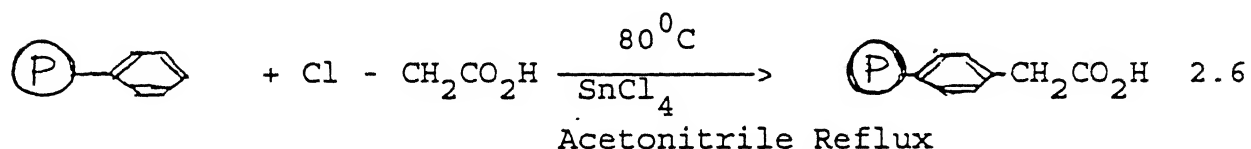2(d) PREPARATION OF QUATERNARY AMMONIUM SALT USING CHLORO CHOLINE CHLORIDE :

6 gms of 12-hydroxy steroly 1,2 amide amine was dissolved in 20 c.c of 1,2 dichloro methane 2.68 gms of chloro choline chloride was dissolved in separate 15 c.c dichloro methane. The solution of amine compound was refluxed at 40^0C and to this under refluxe condition, chloro choline chloride solution was added dropwise over period of 1 hr. This mixture was stirred vigorously for 8-9 hrs under the refluxed condition. After this time the mixture was cooled to room temperature the solvent 1-2 dichloro methane was evaporated at room temperature $(20^0\text{-}30^0C)$ leaving the quaternary ammomium salt as a precipitated. It was filtered ane dried the final product of the quaternary ammonium salt was weight about 7.6 gms.

$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}CH_2CONHCH_2CH_2NH_2 + Cl\text{-}CH_2CH_2\overset{+}{N}(Me)_3\text{-}Cl \longrightarrow$$

$$H_3C(CH_2)_5CH(OH)(CH_2)_{10}CH_2CONHCH_2CH_2NH - CH_2CH_2\overset{+}{N}Me_3Cl \qquad 2.5$$

Formation of quaternary compound ammonium compound was confirmed by I.R. spectroscopy. The frequency of tertiary amine was found 2250 cem^{-1}.
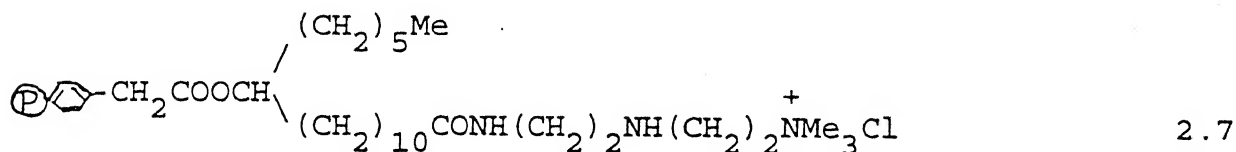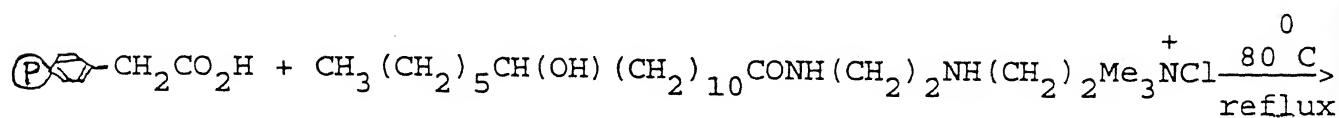
ACETYLATION OF POLYMER BEADS :-

Acetylation of beads was carried using monochloroacetic acid as follows. 5 gms of polystyrene beads was put in benzene (50 c.c) and lewis acid (1-2 gms) $SnCl_4$ was added which serve as catalyst. The mono chloroacetic acid (5 gms) was added and this mixture was refluxed at 80^0C for 24 hrs. This mixture was cooled to room temperature and the beads were separated. This was washed repeatedly with methanol and finallywith acetone. Subsequently it was dried. The overall reaction can be represented by

$$\text{P}-\langle\text{C}\rangle \quad + \quad Cl - CH_2CO_2H \xrightarrow[\substack{SnCl_4 \\ \text{Acetonitrile Reflux}}]{80^0C} \quad \text{P}\langle\text{C}\rangle-CH_2CO_2H \quad 2.6$$

GENERATION OF QUATERNARY AMMONIUM SALT ON POLYMER BEADS :-

5 gms of quaternary ammonium salt of 12-hydroxy stearic acid was dissolved in 20 ml 1-2 dichloromethane. To this, 4.5 gms of acetylated beads were added. This was refluxed at 40^0C. Under refluxed condition, quaternary ammonium salt solution was added dropwise with mild stirring for 1 hr.

$$\text{(P)} \diamondsuit - CH_2CO_2H + CH_3(CH_2)_5CH(OH)(CH_2)_{10}CONH(CH_2)_2NH(CH_2)_2Me_3\overset{+}{N}Cl \xrightarrow[\text{reflux}]{80^0 C}$$

$$\text{(P)} \diamondsuit - CH_2COOCH \underset{(CH_2)_{10}CONH(CH_2)_2NH(CH_2)_2\overset{+}{N}Me_3\,Cl}{\overset{(CH_2)_5Me}{\Big<}} \qquad\qquad 2.7$$

Formation of this compound was confirmed by I.R. spectroscopy. The formation of ester group was confirmed. The frequency value is 1650 cm^{-1}. which was comparble with literature value.

SYNTHESIS OF THE QUATERNARY AMMONIUM SALT OF PHOSPHOTUNGSTIC ACID

8.5 gms of quaternary ammonium salt supported on polymer beads was added to 30 c.c 1-2 dichloromethane, 7 gms of phosphotungstic acid was dissolved in 15 c.c 1-2 dichloromethane to added dropwise over 45 minutes at 30-40^{0}C

lOADING OF PHOSPHOTUNGSTIC ACID IN THE QUATERNARY ONIUM SITES OF POLYMER BEADS :-

Procedure folloed in this thesis adopted from that proposed by Duncan et.al.[18] To a solution of 5 gms ofphosphotungsticacid in 3 c.c distilled water taken in a clean conical flask was added, with vigorous stirring, 40 c.c 30 % aqueous H_2O_2 solution was stirred for 5 hrs. at room temperature and 6 gms of quaternized polymer beads were added to it and kept at room temperature for 48 hrs. without stirred. The peroxo complex separated and dried at low temperature. This compound phosphotungstic acid was confirmed by EPR (Electron Paramagnetic Resonance).

EPOXIDATION OF ALLYL CHLORIDE :-

A procedure followed in this thesis adopted from that proposed by Ischii et.al.[11] Reaction were conducted in a 100 ml conical flask at room temperature. The quaternary ammonium salt of phosphotungstic complex (~ 5 gms) put in chloroform (30 c.c), 20 c.c of H_2O_2 was added and stirring was continued for about 1 hr at room temperature. Then allyl chloride (2.5 ml) was added and mixture was allowed to react with continous stirring. After the reaction the two layers (aqueous and organic phase) separated. The organic layer was washed two -three times with water and analysed by titration procedure.

CONFIRMATION AND ESTIMATION OF α - EPOXIDE BY TITRATION :-

GENERATION OF DRY HCl GAS :-

Generation of dry HCl gas was done by taking 60 gms of NaCl in a 100 ml round bottom flask and adding 50 ml of concentrated sulphuric acid added dropwise to it. The reaction giving HCl is

$$2NaCl + H_2SO_4 \longrightarrow 2HCl + Na_2SO_4 \qquad 2.8$$
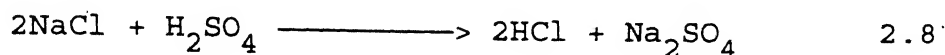
PREPARATION OF PYRIDINIUM CHLORIDE CHLOROFORM SOLUTION :-

Procedure followed as proposed in literature [34] The hydrochlorination reagent is 1 (N) solution of pyridinium in chloroform and is prepared by adding 75 gms of anhydrous pyridine and 400 ml of chloroform in a 1 Liter conical flask. The flask was cooled in an ice bath and dry HCl gas generated above was bubbled into it slowly. At intervals of 2-3 minutes. The HCl flow was stopped only after approximately 35 gms of HCl had been introduced. Then the mixture was warmed to room temperature. To get 1N of solution for titration, a 10 ml of pyridinium chloride chloroform solution was added to a small volume (about 2-3 ml) of water. To determine its strength, this is titrated with standard 0.5 (N) methanolic sodium hydroxide solution using phenolohthalin indicator for end point indication. From this titration,was determined and then the solution was diluted with with chloroform (~ 125 c.c). So that the final strength was approximately 1N.

The α-epoxide was added to a 250 c.c flask, containing 25 c.c of 1(N) pyridinium chloride chloroform solution. The mixture is boiled, under refluxed condition for 30 minutes and then was cooled to room temperature. It is then distilled water using phenolphthalin indicator. The mixture was titrated with standard 0.5 (N) methanolic sodium hydroxide solution to a definite pink colour.

CALCULATION OF PERCENTAGE CONVERSION OF ALLYL CHLORIDE IN THE REACTION MASS :-

The entire reaction mixture (30 c.c) was added to 25 ml of 1(N)pyridinium chloride solution and refluxed at 80^0C - 100^0C temperature for 30 minutes. The mixture is cooled at room temperature and 10 ml of distilled water is added. It is than titrated by 0.5 (N) methanolic sodiun hydroxide solution using phenolphthelin as a indicator. A definite pink colour indicates end point of titration. Volume of titration 47 c.c . The reaction occurring with the epoxide group is

$$CH_2-CH-CH_2-Cl + HCl \xrightarrow[\text{under reflux}]{\text{boil 80-100}^0\text{C}} CH_2(OH)CH(Cl)CH_2-Cl \quad 2.8$$
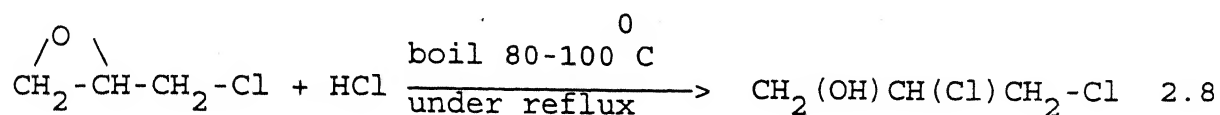
TITRATION FOR BLANK :-

In order to determine the concentration of epoxide functional group it is necessary to carry out blank titration. For this 30 ml of chloroform was added to 25 ml of 1(N) pyridinium chloride solution. This is refluxed at 80^0C - 100^0C temperature for 30 minutes and after that the mixture is cooled to room temperature. To this, 10 ml of water was added and was titrated by 0.5N methanolic sodium hydroxide using phenolphthalin as a indicator.

<u>TEST</u> <u>OF</u> <u>TITERATION</u> <u>PROCEDURE</u> <u>USING</u> <u>STANDARD</u> <u>EPICHLOROHYDRINE</u> :-

Procedure discribed as in literature [34]. Standard 1 ml epichlorohydrine (1.183 gm) was mixed 25 ml of 1(n) pyridinium chloride solution. This mixture was boiled under reflux condition for 30 minutes. The reaction mixture was cooled at room temperature and diluted with 10 ml of distilled water. Using phenolphthalin indicator the mixture was titerated with standard 0.5 (N) methanolic sodium hydroxide solution to a definite pink colour.

RESULTS :-

Volume of titerated for sample = 23.1 c.c

Volume of titeration for blank = 48.8 c.c

Excess titeration reading for blank = (48.8-23.1) = 25.7 c.c

$S_1 V_1 = S_2 V_2$

25.7 x 0.5 = V_2 x 1(N)

V_2 = 12.85 c.c

= 0.01285 Moles of HCl

0.01285 Moles of HCl reacts with 0.01285 moles or 1.189 gm of epichlorohydrine.

This compares very well with the starting amount 1.183 gm of epichlorohydrine. It is thus seen the estimated value lies within 0.5% .

PREPARATION OF POLYANILINE POLYMERIZED WITH AMMONIUM PERSULPHATE

Polyaniline was prepared by oxidation of aniline with ammonium persulphate in an acidic medium as described in litarature [35]. 20.4 grams of aniline is placed in 300 ml 1M Hcl in an ice/water bath with vigorous stirring. Ammonium persulphate [11.5 grams,50.4 mmole] dissolved in 1M Hcl(200 ml) is cooled in an ice/water bath. This solution is added dropwise to the solution of aniline over about 10 minitues with vigorous stirring. When polymerisation starts , the solution of aniline turns dark green and the salt of polyaniline begins to precipitate. After complete addition of ammonium persulphate , the mixture is stirred for additional 2 hours. Polyaniline does not dissolve in the reaction medium and is using a buchner funnel and washed with 1M Hcl(300 ml) ,then with acetonitrile(300 ml) and dried at room tempereture for 24 hours. The amount of polyaniline formed is 4.49 grams.

PREPARATION OF POLYANILINE SUPPORTED COBALT (11) CATALYSIS

Procedure described as in literature [36]. A mixture of polyaniline (4grams) and cobalt acetate (4 grams) is stirred in acetonitrile (50 ml) and acetic acid (50 ml) for 72 hours at room temperature. The reaction mixture is filtered and the solid catalyst washed with acetonitrile until the filterate became colourless. The catalyst is dried at $110^{0}C$-$120^{0}C$.

Table 1: Titration of ReactionMass Catalysed byh Polyaniline Supported Co (II) Acetate Catalyst of Alkenes in presenceof RCHO (R=Me, H) & Molecular O_2

Table 1a. Titration of reaction mass where alkene is allyl chloride

Condition : Pressure = $50kg/cm^2$ (Pure O_2), Temperature = $60^{o}C$ and Room Temp., Time = 24 hrs, Volume of Allyl cholride ≑ 1 ml

Volume of RCHO = 1 ml, Solvent Acetonitrile = 30 ml

RUN NO.	VOLUME OF PYRIDIUM CHLORIDE SOLUTION	VOLUME OF REACTION MASS	VOLUME OF METHANOLIC NaOH	AVERAGE READING
1	20 ML	30 ML	44ML	
2	20 ML	30 ML	44.1 ML	44.05 ML
3	20 ML	30 ML	44.05 ML	

Table 1b. Titration of Blank

RUN NO.	VOLUME OF PYRIDIUM CHLORIDE SOLUTION	VOLUME OF Solvent	VOLUME OF METHANOLIC NaOH	AVERAGE READING
1	20 ML	30 ML	44.1 ML	
2	20 ML	30 ML	44.2 ML	44.07ML
3	20 ML	30 ML	44.05 ML	

Table 1c. Titration of reaction mass where alkene is Styrene

Condition :Pressure = $50kg/cm^2$ (Pure O_2), Temperature = 60^OC and Room Temp.,

Time = 24 hrs, Volume of Styrene = 2 ml

Volume of RCHO = 2 ml, Solvent Acetonitrile = 30 ml

RUN NO.	VOLUME OF PYRIDIUM CHLORIDE SOLUTION	VOLUME OF REACTION MASS	VOLUME OF METHANOLIC NaOH	AVERAGE READING
1	20 ML	30 ML	47ML	
2	20 ML	30 ML	47.1 ML	47.05 ML
3	20 ML	30 ML	47.05 ML	

Table 1d. Titration of blank

RUN NO.	VOLUME OF PYRIDIUM CHLORIDE SOLUTION	VOLUME OF Solvent	VOLUME OF METHANOLIC NaOH	AVERAGE READING
1	20 ML	30 ML	47.1 ML	
2	20 ML	30 ML	47.1 ML	47.08ML
3	20 ML	30 ML	47.05 ML	

CHAPTER-3

RESULT AND DISCUSSION

It has already been explained that epoxidation increases the reactivity of the reagent because almost all epoxides react at considerably milder conditions. Epoxidation of larger molecules is normally carried out using oxygen carrying reagents like hydrogen peroxide ; however it is most a desirable reagent primarily because it forms a two phase mixture with the reactants. In addition to this, H_2O_2 undergoes an autocatalytic breakage into water and oxygen in presence of any surface. This autolysis is known to be accelerated by mettallic surfaces and the reacter should be specially glass dried for this reason. It is mostly because of these reasons, hydrogen peroxide has very few commercial applications.

There has been considerable research being done to replace hydrogen peroxide with molecular dioxygen which has considerable lower activity. This partially arises because it dissloves in the reaction medium in very small amount and when in reference , the use of molecular dioxygen was reported for epoxidation reaction we decided to study the epoxidation allyl chloride and styrene in greater detail. After the occurrence of the reaction is demonstrated, it is important to understand the effect of oxygen pressure, the reaction temperature, product composition and side reactions if any.

We first focussed our attention on synthesis of polyaniline which is a conducting polymer, but unfortunatly does not dissolve in any medium. The molecular weight of the polymer could be calculated only indirectly and literature reports two different techniques for materials of low and high molecular weights and it was possible for us to synthesize both these. Later it was seen that it made no difference to the conversion of allyl chloride or styrene.

After preparing polyaniline, we followed reference [36] for loading of cobaltous chloride. The loading was straight forward and was confirmed by the gain in weight of the catalyst. This weight did not change during the reaction, this way confirming that there was no leaching of metal. The literature reported that the epoxidation occurred at the room temperature in presence of an aldehyde but the epoxidation of allyl chloride did not occur at the room temperature under the condition reported. Since allyl chloride boils at ~ 40°C , in order to carry out reaction at higher temperatures, we used a rocking type pressure vessel. We than studied the effect of oxygen pressure and temperature and we showed that the gas chromatograph showed no conversion.

The column used in the GC was SE - 20 and we thought that there may have been difficulty in the separation due to type of the column used. Several other column were tried and we were surprised that we did not get any result. To further confirm we directly titrated the epoxide groups and we still got negative results. The experimental findings are summarized in Table 1.

In view of our inability to use molecular oxygen directly for epoxidation, we decided to use hydrogen peroxide again as the source of oxygen. The work of Shaneeth had already demonstrated that HPA loaded on polymer beads did not work partially because the beads promoted autolysis of hydrogen peroxide and partially because they preferentially remained in the organic medium. In view of his findings, we wished start with material which is a bifunctional surfactant molecular having tendency to stay atthe interface. For this purpose, we chose to work with 12-hydroxy stearic acid in which the carboxylic acid moity would be used for holding the HPA and the hydroxyl group to hang the molecule on a suitably functionalized surface.

We once again decided to work with crosslinked styrene-divinyl benzene copolymer beads as the catalysis support. We functionalized it using monochloroacetic acid as described in the experimental section. Chloroacetic acid highly corrosive and normally the beads break down to smaller particles. As a result in order to preserve the beads, acetonitrile medium was chosen so that at any time the concentration of chloroacetic acid is small. Due to this reaction the beads undergo a change in colour and the IR of the production clearly showed an ester functional group. With these indications, we assumed that the reaction occurred smoothly.

To hold the heteropolyacid (HPA) on 12-hydroxy stearic acid, we first convertwd the latter to acid chloride using thionyl chloride. The solid reactant dissolves in the medium and for the

refluxing at 40°C we used dichloromethane solvent. The entire solution burns black and the reaction occurs over a period of 12 hours. It is extremelyimportant that unreacted thionyl chloride be removed and for this the through washing with distilled water several times as done. It is now desired that single substitution with ethylene diamine is done and for this reason, the acid chloride solution of hydroxystearic acid be slowly added in excess of ethylene diamine. Since ethyene diamine is tetra functional, in the limit four acid chloride molecules can expected limited solubilties.

As soon as the acid chloride solution as added to the excess of ethylene diamine, the precipitate appears. Since the reaction temperature is small, it is expected to form a linear chain and the final product is found to dissolve in dichloromethane, DMSO and DMF, 1,2 di chloroethane, acetonitrile etc. The tertiary ammonium chloride salt of this compound was formed by reacting this with chloro choline chloride in dichlromethane medium. The reaction runs smoothly and the final product is confirmed by the IR which clearly shows the tertiary ammonium salt. This also complexes with HPA, and is reacted with the polymer bead having -CH$_2$COOH functional group, this way giving us the described catalyst. The only problem is that the catalyst paricle breaks into smaller ones and it is required that the reaction conditions should be suitably reworked round the present strategy to determine optimal conditions.

Finally we carried out epoxidation of allyl chloride. Allyl chloride has high vapour pressure and low boiling point and the reaction is to be run for long time (about 12 hours). During the reaction, there is a substantial loss of reactant by evaporation if the vessel is kept open to atmosphere. The second point which must be observed is the autolysis of hydrogen peroxide. In normal conditions, the unmodified polymer beads cause considerable breakage of H_2O as can be seen by vigorous bubbling of oxygen. In presence of the modified beads, this autolysis was considerably reduced and in this regard, it was an achievement. On running the reaction, for 12 hours within a closed reactor, the reaction was found to occur and the titration of the reaction mass gave about 36 % which was decent.

CHAPTER -4

CONCLUSIONS

Most of the studies on epoxidation of allyl chloride with hydrogen peroxide oxidant was based on using the catalyst heteropolyacid salt of cetyl pyridinium (or n-butyl) bromide. The major disadvantage has been that the catalyst salt was soluble in water and after the homogenous reaction was complete, the catalyst could not be recovered. In the earlier work of Shaneeth et.al, surfaces of polystyrene-divinyl benzene copolymer beads and silica gel were chemically modified to have tertiary ammonium (or phosphonium) groups to form salt with HPA. Experimental work revealed that these catalysts either gave accelerated autolysis of H_2O_2 and they did not stay the organic interface layer. To over come both these effects, in this thesis , it was decided to use a bifuctional surfactant molecule so that at one end it is bound to a support. The other end of this molecule is suitably modified to have tertiary ammonium (or Phosphonium) group to form the HPA salt.

The bifunctional surfactant molecule chosen for this purpose has been 12-hydroxy stearic acid. We have first decided to modify the molecule to have tertiary ammonium salt as follows. The surfactant molecule was reacted with thionyl chloride to give its acetyl chloride at room temperature as confirmed by I.R. It was subsequently reacted with ethylene diamine followed by

reaction with chloro choline chloride. The styrene divinyl benzene copolymer beads were prepared using standerd technique and then these beads were reacted with monochloro acetic acid to give -(CH$_2$COOH) groups on their surface. These were reacted with thionyl chloride to give acid chloride functional groups followed by its reaction with the modified surfactant formed earlier. The modified polymer beads were then loaded with HPA to give the desired catalyst.

The catalyst so prepared was used for epoxidizing allyl chloride with H$_2$O$_2$ as the reagent. It was observed that the catalyst gave considerably reduced autolysis of hydrogen peroxide and the beads stayed at the interface. The use of GC for measuring conversion could not be worked out because we could not find a suitable column. As a result of this we used the standard titration technique which gave a 36% epoxidation, which was very heartening result. There is still a need to study the reaction in more detail.
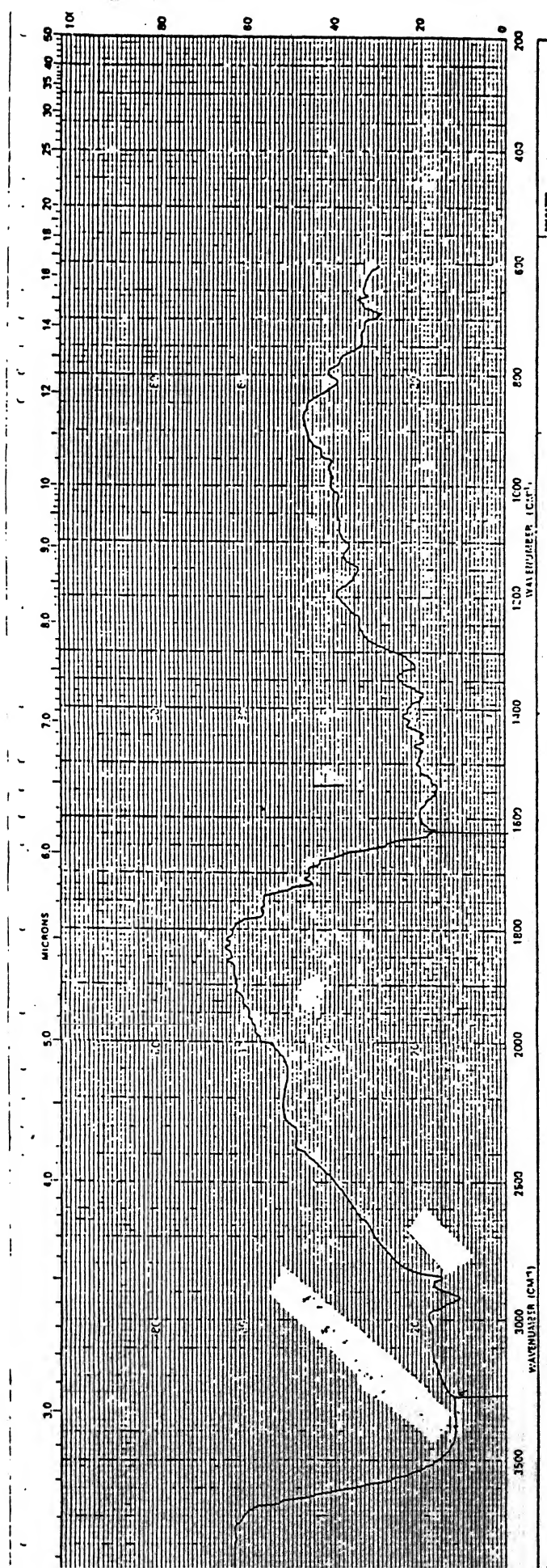
APPENDIX A

INFRA RED SPECTRA

&

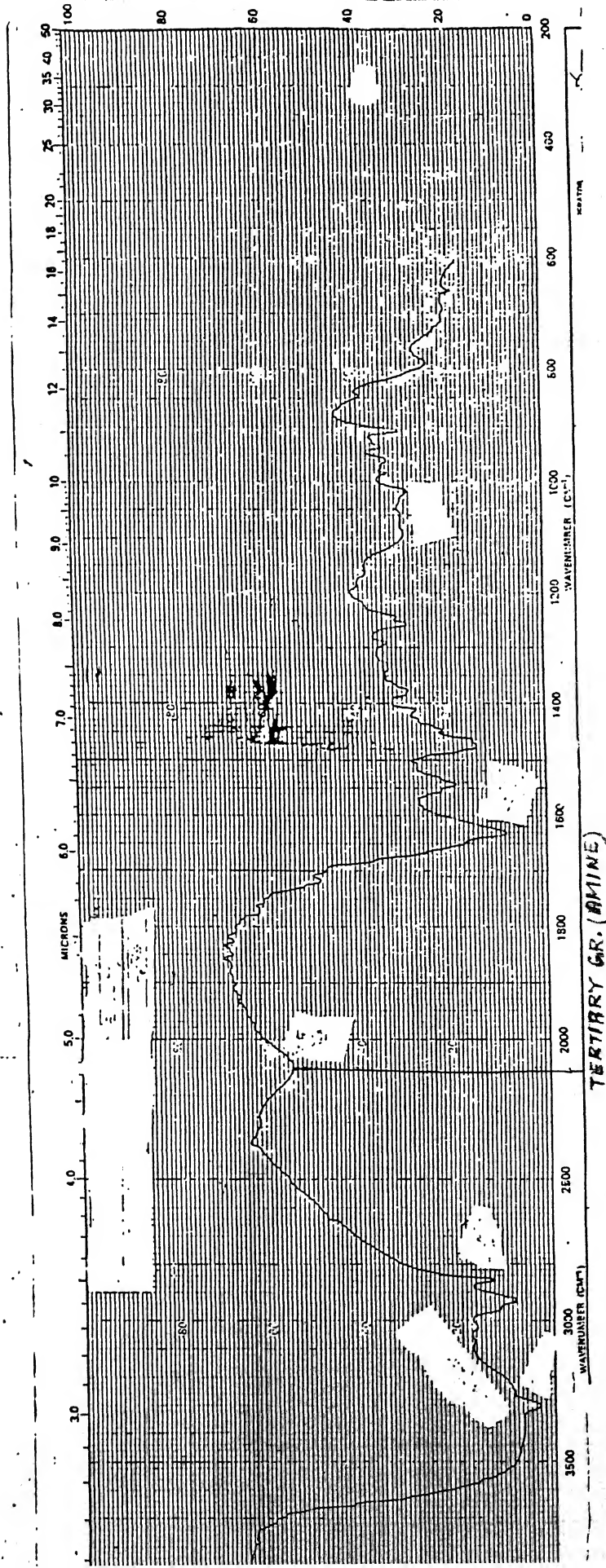## ELECTRON PARAMAGNETIC RESONANCE SPECTRA
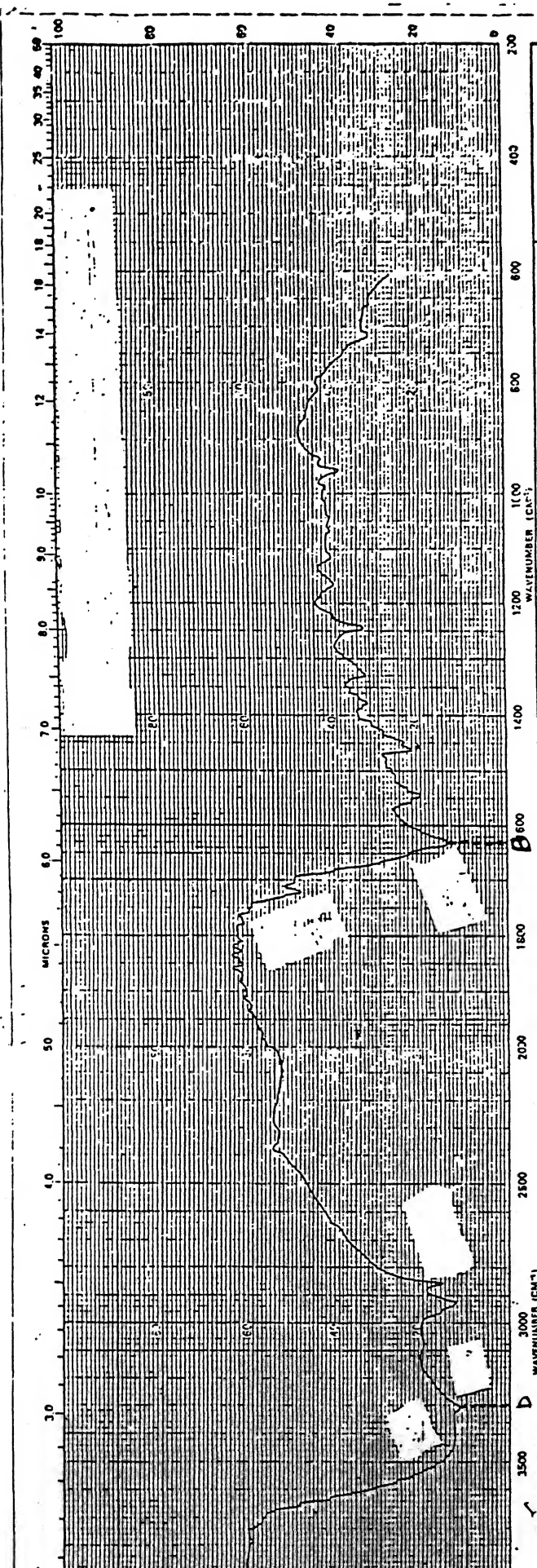
A1: Infra Red Spectrum of the compound obtained from by reacting
with 12-hydroxy Steroyl Chloride(Excess) + Ethylene diamine

D: Frquency value of OH

B: Frequency value of CONH

40a

A2:　　Infra Red Spectrum of the compound obtained from by reacting with 12-hydroxy Steroyl Chloride + Ethylene diamine (Excess)

40_b
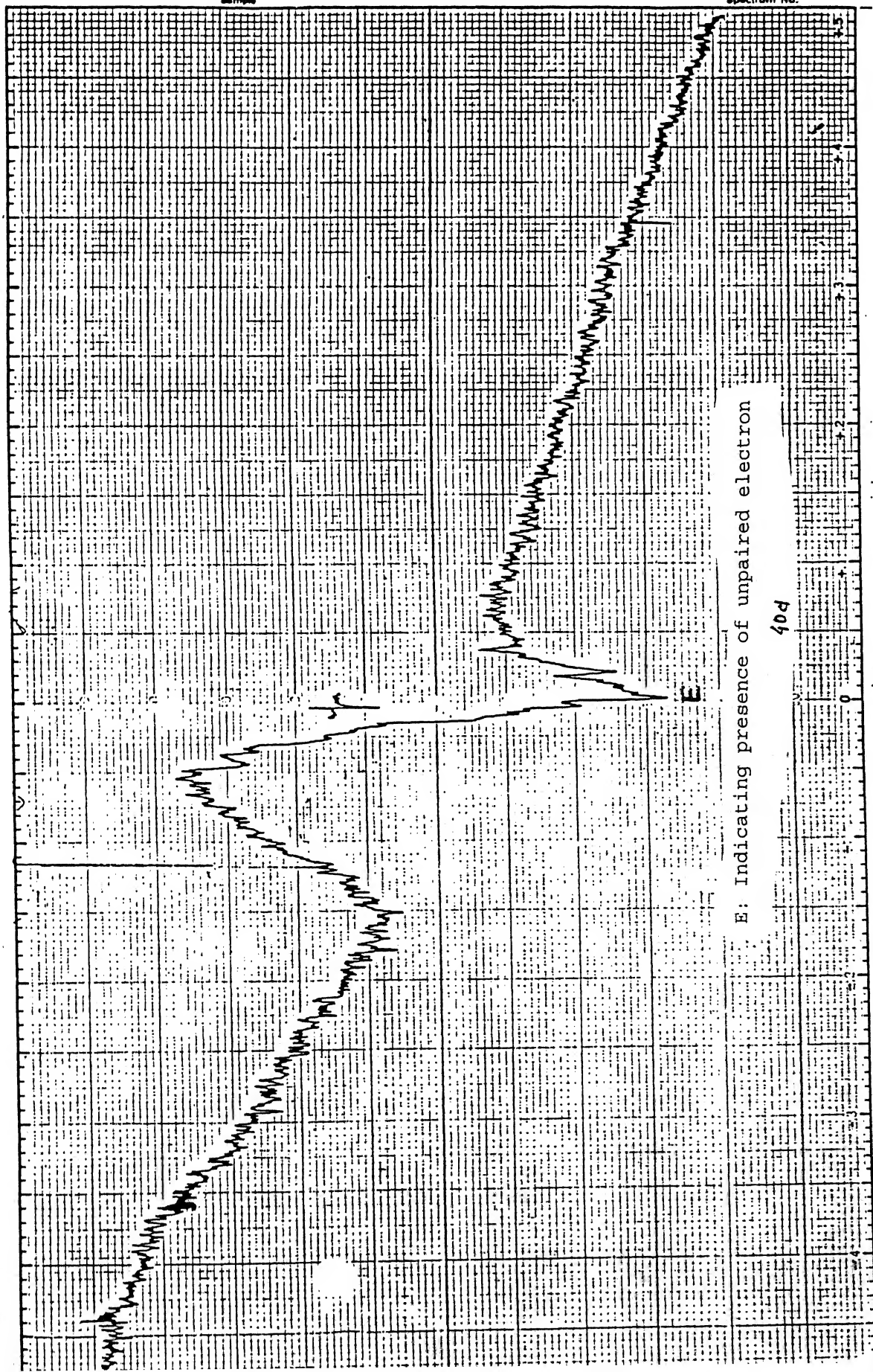
A3: Infra Red Spectrum of the Quaternary Ammonlum Salt of Polymer Supported Steroyl 1',2'. Amide amine and Chloro Choline Chloride.

40c

EPR CHART A

Recordwel ®

Sample

Spectrum No.

A4 : Electron Paramagnetic Resonance Spectrum of Polymer Supported - $PO_4[WO(O_2)_2]_4$ (Peroxo Complex)

E: Indicating presence of unpaired electron

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